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Estimating Herbicide Partition Coefficients from Electromagnetic Induction Measurements

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ABSTRACT

A potential method for reducing pesticide leaching is to base application rates on the leaching potential of a specific chemical and soil combination. However, leaching is determined in part by the partitioning of the chemical between the soil and soil solution, which varies across a field. Standard methods of measuring the pesticide-soil partitioning coefficient (K_d) are too expensive and slow for routine field mapping. Therefore, alternative methods for mapping K_d must be found if variable application methods are to be successful. We investigated the use of noncontacting electromagnetic induction measurements as surrogate measures of K_d . We measured the partition coefficient for atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), apparent electrical conductivity by electromagnetic induction (E_m), and mass fraction of soil organic carbon (f_{oc}) on a 250 by 250 m grid with a 25 m spacing. Both K_d and f_{oc} were lognormally distributed, while E_m was poorly described by either a normal or lognormal distribution. Maps of the measured parameters showed similar spatial patterns, having low values on well-drained soils and high values on poorly drained soils. Correlation coefficients between K_d and E_m and K_d and f_{oc} were 0.575 and 0.686, and showed distinct spatial patterns. Spatial structure as indicated by correlograms indicated that each parameter was spatially dependent to distances of about 80 m. Simple relationships of $K_d = 176 f_{oc}$ and $K_d = \exp(0.0336 E_m)$ were found between the data. Maps of K_d estimated from f_{oc} or E_m were similar to measured K_d , but more diffuse. Electromagnetic induction measurements failed to predict the observed high K_d values. The advantage of using E_m measurements to map K_d is that it is a rapid, easy, and inexpensive method once it has been calibrated.

ONE OF THE DIFFICULTIES in predicting the fate of field-applied pesticides is that there is relatively little information concerning "the intrinsic variability in soil properties or parameters...that dictate pesticide

persistence" (Rao and Wagenet, 1985). For example, the affinity of a chemical to sorb to the soil matrix can vary across a field (Rao et al., 1986; Wood et al., 1987; Cambardella et al., 1994) or even spatially within the same map unit (J.M. Novak et al., unpublished data). And yet Loague et al. (1990) found that sorption can be the predominant process contributing to the variability of pesticide mobility across the landscape.

The partitioning of an herbicide between the solution and soil phases is often represented by (Freeze and Cherry, 1979):

$$s = K_d c \quad [1]$$

where s is the sorbed concentration on the soil (mg/kg), c is the solution concentration (mg/L), and K_d is the partition coefficient (L/kg). Standard methods for measuring K_d (Novak et al., 1994) are time consuming and require costly, specialized equipment.

Due to the expense and time required to measure partition coefficients for combinations of specific soils and chemicals, the coefficients are often estimated from related soil properties. In particular, organic C content is commonly used since this soil fraction strongly interacts with nonionic herbicides (Bailey and White, 1970). The relationship between soil organic C mass fraction (f_{oc}) and K_d can be expressed as:

$$K_d = K_{oc} f_{oc} \quad [2]$$

where K_{oc} (L/kg) is the coefficient of proportionality.

Although not a perfect correlation, this approach has proven to be satisfactory for many purposes (Rao and Davidson, 1980). However, if we wish to characterize the spatial variability of K_d over a field or larger unit, even this approach is cumbersome since measuring the organic C content of a large number of samples is not a trivial task. Alternative, more easily measured surrogate parameters of K_d are needed.

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Electromagnetic induction meters have been used for many years in the geological sciences (Zalasiewicz et al., 1985). The meter produces an oscillating magnetic field that induces electrical currents in the soil, which in turn create a secondary magnetic field that is measured by the meter (McNeill, 1980a). By using electromagnetic induction, the meter need not contact the ground to measure apparent electrical conductivity. Recently, these meters have been used in soil science to measure soil salinity (Rhoades and Corwin, 1981), soil water content (Kachanoski et al., 1988), soil clay content (Williams and Hoey, 1987), and soil cation exchange capacity and exchangeable Ca and Mg (McBride et al., 1990). In addition, electromagnetic induction meters have been used successfully to determine field-scale leaching rates of solutes (Slavich and Yang, 1990).

The measured electrical conductivity is a complicated function of soil clay mineralogy, water content, and dissolved solute composition and concentration (McNeill, 1980a). Except for clay mineralogy (Laird et al., 1992), these factors are not normally expected to interact with herbicide partitioning. However, in many regions of the country, vast areas have soils formed from common parent materials, where the primary driving factor determining soil water content and solution composition is the soil drainage class. On average, we would expect soils to have higher water contents and higher concentrations of dissolved solids in poorly drained areas than in well-drained areas. Similarly, soil organic C content is intimately related to drainage class, with higher contents in poorly drained areas and lower contents in well-drained areas. Thus, while electrical conductivity does not respond directly to changes in soil-herbicide partitioning, we expect both electrical conductivity and soil organic C to respond to the same forcing function—soil drainage.

In this study we tested the hypothesis that within a field of soils formed from the same parent material, electrical conductivity as measured by electromagnetic induction can be used as a surrogate measure of soil-herbicide partitioning. Atrazine was used as the prototype herbicide. As a basis of comparison, we also estimated K_d from organic C content and compared the two techniques for estimating not only the magnitude of K_d , but also the spatial pattern of K_d within the field.

MATERIALS AND METHODS

Measurements were made in a 32-ha field within the Walnut Creek watershed in central Iowa. A detailed description of the soils, geology, and farming practices within the watershed can be found in Sauer and Hatfield (1994). The landscape within the watershed is characterized by gently swell-swale relief of several meters (Daniels and Handy, 1966). Surface drainage is poorly developed resulting in numerous closed depressions or potholes that have been extensively tile drained in the past 100 yr.

Soils within the watershed were formed from till of the Cary substage of the Wisconsin glaciation. The toposquence of soils within the field range from well-drained Clarion loam (fine-loamy, mixed, mesic Typic Hapludolls), to the somewhat poorly drained Nicollet loam (fine-loamy, mixed, mesic Aquic

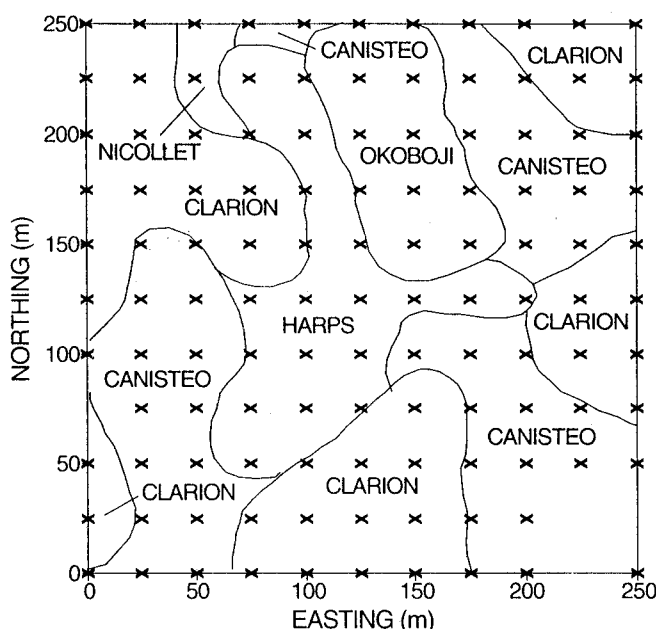


Fig. 1. Plot of E_m measurement and soil sampling locations superimposed on the soil map.

Hapludolls), to the poorly drained Canisteo loam (fine-loamy, mixed [calcareous], mesic Typic Haplaquolls), Harps loam (fine-loamy, mesic Typic Calciquolls), and ending with the very poorly drained Okoboji silty clay loam (fine, montmorillonitic, mesic Cumulic Haplaquolls) (Fig. 1).

Before planting in 1992, a grid was laid out across a 250 by 250 m area in the southern half of the field (Fig. 1). Grid spacing was 25 m in both the east-west and north-south directions. Additional grid points were established at closer spacings but were not included in this study. Within 1 m of each grid point, three 6-cm diam. cores were taken to a depth of 15 cm and composited for analysis. The mass of organic C expressed as a fraction of the total soil mass (f_{oc}) was measured using dry combustion methods with a Carlo-Erba NA1500 NCS elemental analyzer (Haake Buchler Instruments, Paterson, NJ¹) after carbonates had been removed with 2 M H_2SO_4 .

Atrazine sorption was determined on duplicate 4-g samples of air-dried soil that had passed a 2-mm sieve. Soil was equilibrated with 15 mL of solution containing 1.5 mg/L atrazine dissolved in 0.01 M $CaCl_2$ for 72 h. The solution was then centrifuged and atrazine in the supernatant analyzed with an HPLC as outlined by Novak et al. (1994). Details of the grid establishment and analysis for f_{oc} , K_d , and numerous other chemical, physical, and biological properties of the soil can be found in Cambardella et al. (1994).

At the same time soil samples were collected, apparent electrical conductivity measurements (E_m) were made with an EM38 electromagnetic induction meter (Geonics Limited, Ontario, Canada). A single reading was made at each grid point with the meter in the vertical dipole orientation and 20 cm above the soil surface. Readings were taken with the meter suspended above the soil surface rather than on the surface so that the results from this study could be compared directly to a companion study where the meter was towed across the field on a boom. The EM38 integrates over a distance

¹ Trade and company names are used for the benefit of readers and do not imply endorsement by the USDA.

Table 1. Descriptive statistics and correlation coefficients for 117 measurements of apparent electrical conductivity (E_m), atrazine partition coefficient (K_d), and mass fraction organic C (f_{oc}).

Property	Mean	Median	SD	Correlation	
				f_{oc}	K_d
E_m (mS/s)	41.0	41.8	13.0	0.765	0.575
K_d (L/kg)	4.94	4.61	1.86	0.686	
f_{oc}	0.0280	0.0274	0.0100		

approximately equal to its length of 1 m and over a depth of approximately 3 m, although the measurement is mostly influenced by properties in the 0 to 1-m depth increment (McNeill, 1980b).

A vertical rather than horizontal orientation was used so that slight variations in the spacing between the meter and soil surface would have minimal effect on the readings (McNeill, 1980b). A horizontal orientation may have resulted in values better correlated to the surface properties measured for this study since the instrument is more sensitive to shallow soil properties in this orientation. However, readings in the horizontal orientation are extremely sensitive to variations in the meter to ground spacing, which would have introduced spurious errors when being towed.

Descriptive statistics and regressions were computed using standard methods (Snedecor and Cochran, 1967; Draper and Smith, 1966). Correlograms were calculated using the method described in Davis (1973). Contour maps of the values were produced using Surfer software (Golden Software, Golden, CO) based on a 41 by 41 grid produced through a linear kriging interpolation procedure embedded within the software.

Correlation maps were created by calculating the individual correlation values at each grid point

$$r_{i,j} = (x_{i,j} - \bar{x})(y_{i,j} - \bar{y}) / (s_x^2 s_y^2)^{1/2} \quad [3]$$

where $x_{i,j}$ and $y_{i,j}$ are values of f_{oc} , K_d , or E_m at the i, j grid location; \bar{x} and \bar{y} are the grid means; and s_x^2 and s_y^2 are the variances. The traditional correlation coefficient is by definition the sum of $r_{i,j}$ over all grid points and divided by the total number of grid points (Snedecor and Cochran, 1967).

RESULTS

Measurements at only 117 of 121 grid points were used because standing water in the southeast corner of the field prevented access to three locations and the fourth measurement was lost. The K_d values for atrazine ranged between 1.74 and 10.92 L/kg (Table 1), with the sample being positively skewed (mean > median). The f_{oc} fraction ranged between 0.0123 and 0.0556 and was also positively skewed. Both K_d and f_{oc} were better described by lognormal distributions than normal distributions (Fig. 2) as determined by the Kolmogorov-Smirnov test and the D'Agostino-Pearson test (Cambar-della et al., 1994).

The E_m values ranged from 20.4 to 65.4 mS/m. These values are only relative, however, and are not direct measures of the true soil electrical conductivity (Lesch et al., 1992). The E_m data were not described well

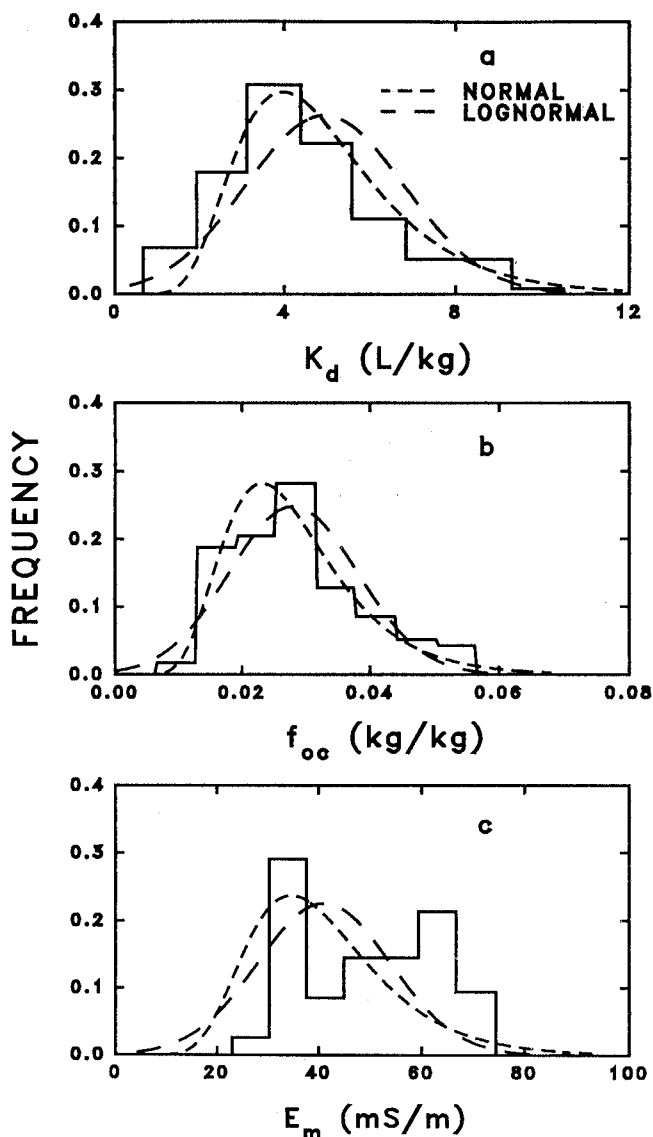


Fig. 2. Histograms and fitted normal and log-normal distributions for (a) atrazine K_d ; (b) soil organic C fraction, f_{oc} ; and (c) apparent electrical conductivity, E_m .

by either normal or lognormal distributions (Fig. 2), although the relative difference between the mean and median was less for the untransformed data.

The spatial distribution of each parameter over the gridded area is shown in Fig. 3. Each parameter showed lower values in areas of the field mapped as well-drained Clarion loam and higher values in the area mapped as very poorly drained Okoboji mucky silt loam. This agrees with our hypothesis that all three parameters should be correlated with drainage class.

Although the plots in Fig. 3 are useful for making qualitative comparisons between the distributions of the three parameters, quantitative comparisons are difficult. However, by plotting the distribution of the correlation statistic, $r_{i,j}$, a quantitative comparison of the spatial pattern of correlation between the different parameters is possible. In Fig. 4, values greater than 0 indicate regions where the two parameters are positively corre-

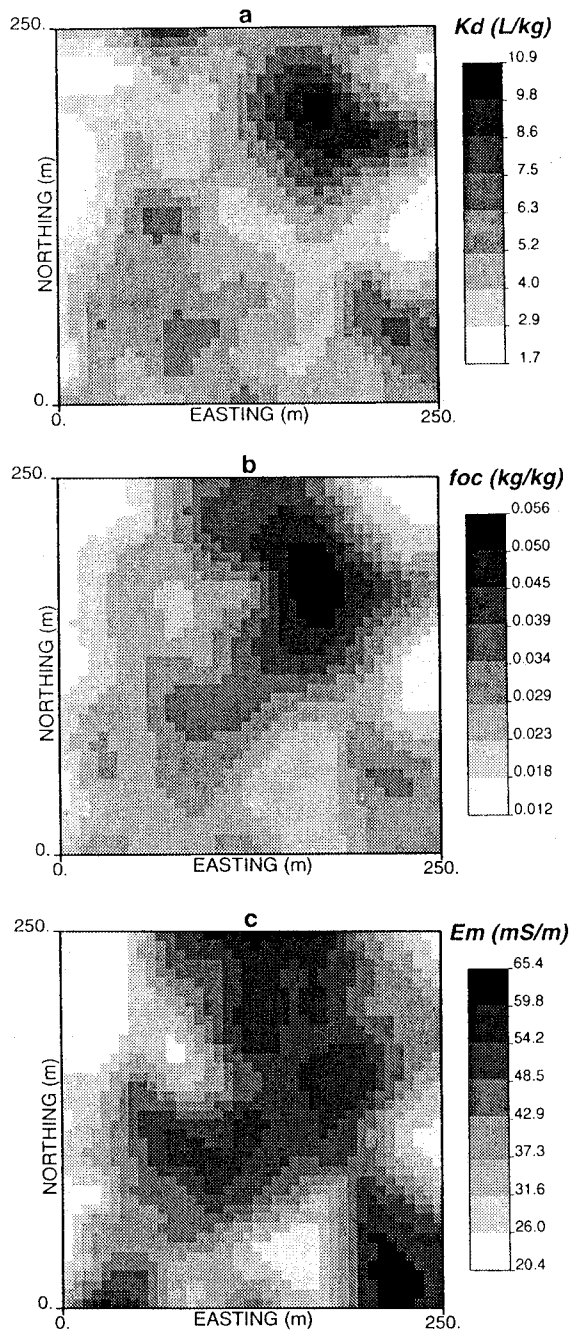


Fig. 3. Spatial distribution of (a) atrazine K_d ; (b) soil organic C fraction, f_{oc} ; and (c) apparent electrical conductivity, E_m .

lated (i.e., deviation for both parameters are either greater than or less than their mean value). Regions of negative correlation indicate that values for one parameter exceed its mean while values for the second are less than its mean.

Very similar patterns are found in both correlation maps, with E_m and K_d being positively correlated across 73% of the area and K_d and f_{oc} positively correlated across 75% of the gridded area. Figure 4 also shows that the lack of correlation is not random but is clustered onto similar areas of the field in both comparisons. The large area of negative correlation in the center of the

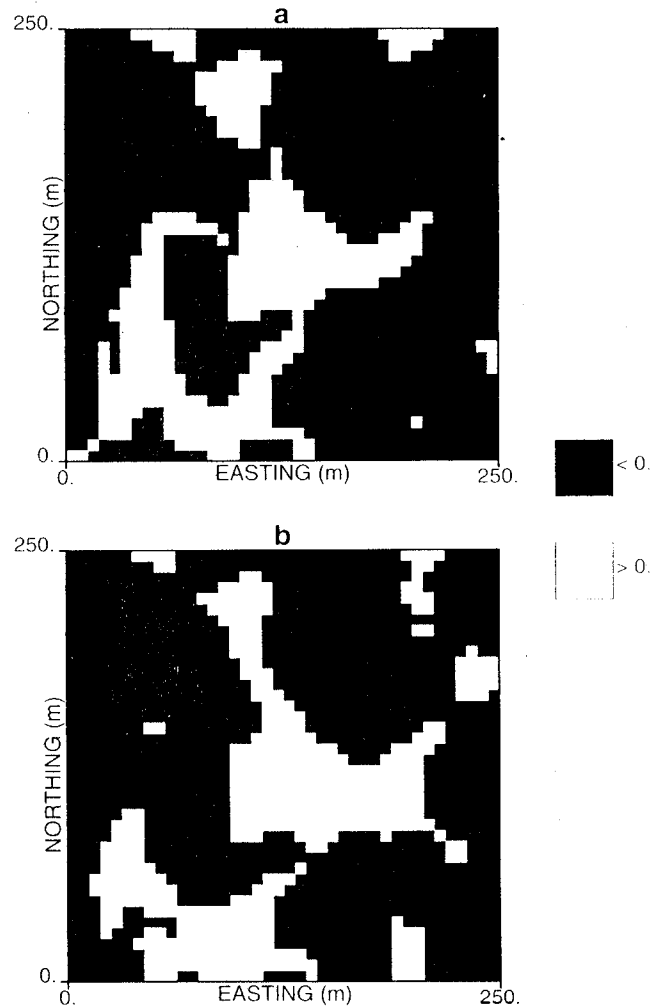


Fig. 4. Correlation map between atrazine K_d and (a) soil organic C fraction, f_{oc} ; and (b) apparent electrical conductivity, E_m .

grid corresponds fairly well with the Harps map unit (Fig. 1). This area of negative correlation may reflect properties of the Harps soil since it is the only soil within the grid with a calcic surface horizon. Atrazine sorption affinity has been shown to decrease with increasing pH (Yamane and Green, 1972). Thus, the observed interaction with the calcic horizon may merely be a function of pH, since the Harps soil samples had a higher average pH than samples from all other map units (J.M. Novak et al., unpublished data).

In addition to similar spatial patterns, the spatial structure of these three parameters is almost identical, as indicated by their correlograms (Fig. 5). The correlograms show a spatial dependence between measurements for each parameter to distances of about 80 m. Again this indicates that the three parameters are responding to the forcing function of soil drainage that varies across the field.

Given the similar spatial patterns, spatial structure, and positive correlation between the parameters, it appears likely that K_d can be successfully estimated from either f_{oc} or E_m . The partition coefficient was calculated by regressing the K_d values vs. the f_{oc} values using linear

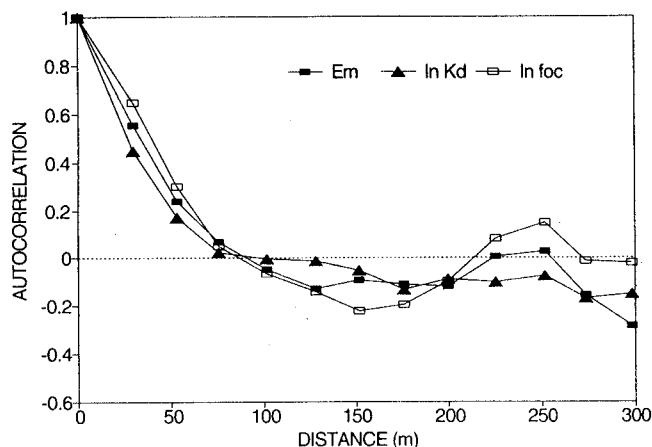


Fig. 5. Correlogram for atrazine K_d ; soil organic C fraction, f_{oc} ; and apparent electrical conductivity, E_m .

least sum-of-squares. The resulting value for K_{oc} was 176 L/kg with a sum-of-squares of 240 L²/kg².

An analogous regression was performed between K_d and E_m . However, since the values were lognormally distributed while the E_m values were better described by a normal distribution, the expression equivalent to K_{oc} is $\ln K_d = \alpha E_m$ or $K_d = \exp(\alpha E_m)$, where α was found by nonlinear regression to be 0.0336. The resulting equation gave a sum-of-squares of 443 L²/kg² or about double that for K_{oc} .

Estimates of K_d from both equations are plotted vs. measured K_d in Fig. 6. Both estimates fall along the 1:1 line with similar scatter except near high K_d values. However, f_{oc} gives a better estimate of K_d at the higher K_d values than does E_m , which accounts for much of the smaller sum-of-squares.

Perhaps more important than overall agreement between calculated and estimated K_d values is whether or not the calculated values show the same spatial patterns as the measured. We plotted the spatial distribution of calculated K_d values in Fig. 7. Compared to the measured K_d values (Fig. 3), both calculated distributions are more diffuse and do not reach the maximum values measured

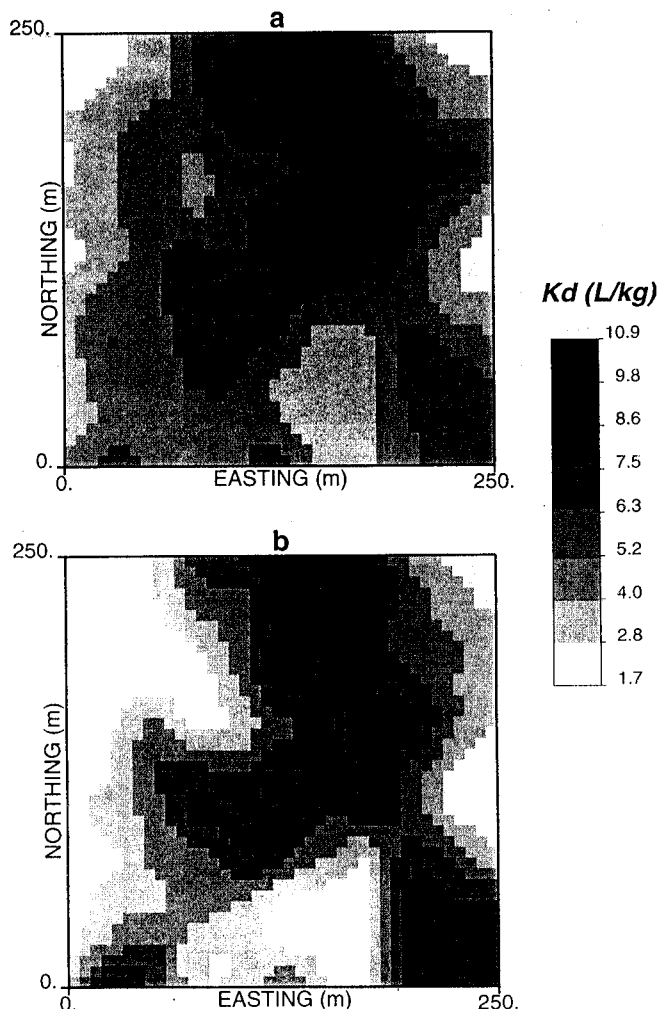


Fig. 7. Map of atrazine K_d values predicted from (a) soil organic C fraction, f_{oc} ; and (b) apparent electrical conductivity, E_m .

within the Okoboji map unit (Fig. 1). However, both calculated distributions accurately recreate the low values of K_d indicative of the better drained Clarion map units.

Quantitative comparisons can be made between the spatial distribution of measured and calculated K_d values by subtracting the calculated from the measured and mapping the residuals (Fig. 8). Under estimations from E_m data of 3 L/kg or more are concentrated within the pothole area and the lower southwest corner of the grid. In contrast, calculations from f_{oc} greatly underestimate K_d only in limited areas along the northern boundary of the grid. Estimates based on f_{oc} and E_m both over estimate K_d in the center of the grid area due to the lack of correlation in this area (Fig. 4).

Overall E_m measurements provided reasonable estimates of K_d although not as accurate as the standard procedure of estimating K_d from f_{oc} . Spatial patterns for estimated K_d values were also similar to measured patterns although more diffuse and estimates based on f_{oc} were closer to measured values in the regions of high K_d . The real advantage to using E_m measurements to estimate K_d , however, is in the speed and ease of making many measurements over a wide area. Measurements of E_m over the grid were made in about an hour, while f_{oc}

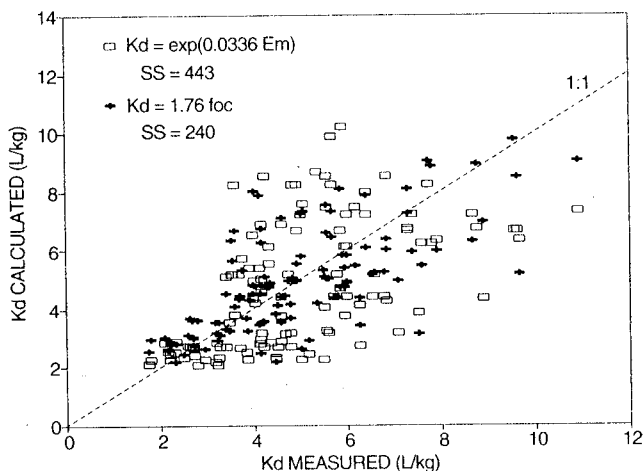


Fig. 6. Atrazine K_d values predicted from soil organic C fraction, f_{oc} ; and apparent electrical conductivity, E_m .

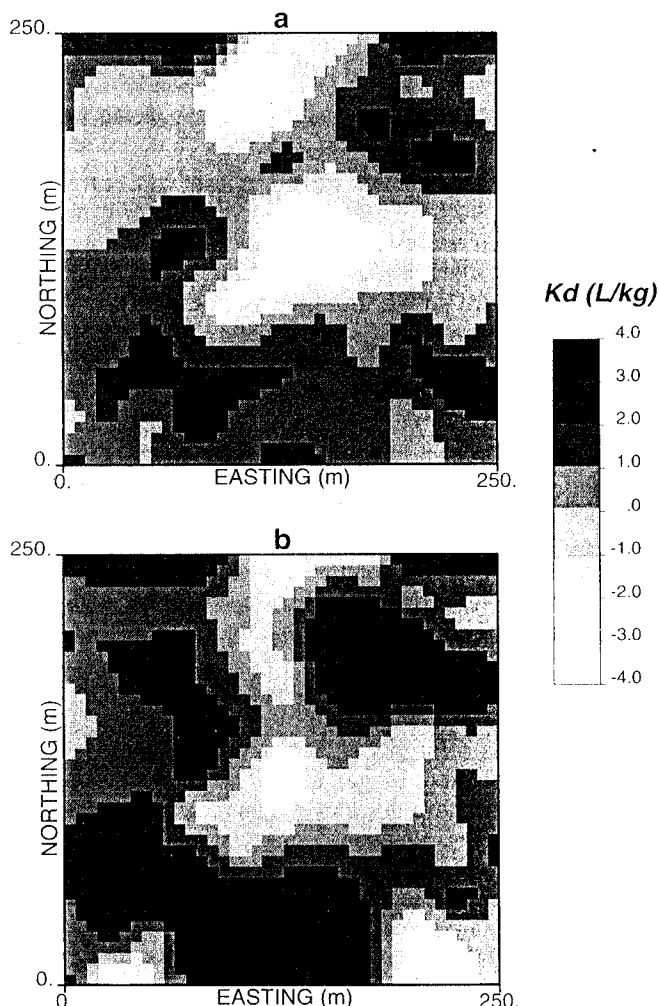


Fig. 8. Map of differences between measured atrazine K_d and K_d values estimated from (a) soil organic C fraction, f_{oc} ; and (b) apparent electrical conductivity, E_m .

determinations took many days of field and laboratory effort. Once calibrated, maps of K_d estimated from E_m surveys will be useful in determining the leaching potential of herbicide applications for specific areas in fields.

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